

TN 295

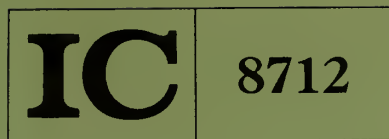
.U4

RI-8712

1976







36.04

Bureau of Mines Information Circular/1976



XRF4—Computer Programing for X-Ray Analysis



UNITED STATES DEPARTMENT OF THE INTERIOR

XRF4—Computer Programing for X-Ray Analysis

By Harold E. Marr III

College Park Metallurgy Research Center, College Park, Md.



UNITED STATES DEPARTMENT OF THE INTERIOR
Thomas S. Kleppe, Secretary

U. S. **BUREAU OF MINES**
" **Thomas V. Falkie, Director**

700

TN 295

U 4

RI-8712

1976

This publication has been cataloged as follows:

Marr, Harold E

XRF4—computer programing for X-ray analysis, by Harold E. Marr III. [Washington] U.S. Bureau of Mines [1976]

32 p. illus., tables. (U.S. Bureau of Mines. Information circular 8712)

1. X-rays—Computer programs. I. U.S. Bureau of Mines. II. Title. (Series)

TN23.U71 no. 8712 622.06173

U.S. Dept. of the Int. Library

CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	1
Application of the computer program XRF4.....	2
Example 1.--Iron and copper in aluminum alloys.....	3
Input information.....	3
Program operation.....	4
Example 2.--Iron-nickel-chromium alloys.....	9
Conclusions.....	13
Appendix A.--STEP options.....	14
Appendix B.--Program modifications.....	16
Appendix C.--Variables for XRF4.....	17
Appendix D.--Models for interelement correction.....	20
Appendix E.--Listing of XRF4.....	25

ILLUSTRATIONS

1. Input format for example 1.....	3
2. Output for example 1.....	5
3. Input data for example 2.....	10
4. Output for example 2, Fe-Ni-Cr alloys.....	11

TABLES

1. Iron and copper in aluminum alloys.....	2
2. Comparison of results from six procedures using Rasberry-Heinrich Fe-Ni-Cr.....	10

XRF4-COMPUTER PROGRAMING FOR X-RAY ANALYSIS

by

Harold E. Marr III¹

ABSTRACT

The computer program XRF4 was designed by the Bureau of Mines to provide for the calculation of several different interelement correction procedures in X-ray fluorescence analysis, including Lachance-Traill, Rasberry-Heinrich, and Claisse-Quintin procedures. The program was written in the BASIC language for timesharing application, and a conversational interaction with the computer is employed during operation. This report presents test problems using data for iron-nickel-chromium alloys and aluminum alloys and directions for use of the program.

INTRODUCTION

Commercial timesharing computer services have made telephone access to large digital computers available to everyone. Many universities and private corporations have installed timesharing capabilities in their own computer centers. Most of the operations are supported by versatile software systems that have flexible data-handling capabilities. At the Bureau of Mines Metallurgy Research Center in College Park, Md., chemists and technicians have been effectively using timesharing computer systems for several years, both for routine analytical service work and for sophisticated computations from more complex research problems.²

A mathematical analysis of the intensity-composition relationship in X-ray analysis was developed by Sherman³ and expressed as a set of explicit closed formulas. Generalization of these equations to mixtures with more than three components is difficult. Therefore, a number of simplified

¹Research chemist.

²Gabler, R. C., R. E. Brown, and J. G. Haymes. A Computer Program for AA Data Processing. Am. Lab., February 1971, pp. 10-16.

Marr, H. E. Mathematical Smoothing of Digitized X-Ray Spectra. BuMines IC 8553, 1972, 15 pp.

_____. Six Models for Interelement Correction in X-Ray Analysis. Advances in X-Ray Analysis, v. 19, 1975, pp. 167-180.

³Sherman, J. The Theoretical Derivation of Fluorescent X-Ray Intensities From Mixtures. Spectrochim. Acta, v. 7, 1955, pp. 283-306.

approximations have been attempted to correct for absorption-enhancement effects in X-ray analysis. The many empirical methods for interelement correction are variations of a few types of equations. Six of these equations have been developed into simple models that have been conveniently programed into a single package for X-ray analysis using a remote-access timesharing computer. The models in the program XRF4 are described in appendix D.

This Bureau of Mines Information Circular is intended to document the program XRF4 and explain its usage. XRF4 was written in the BASIC language and is operational on the General Services Administration GE 435 computer at the Atlanta (Ga.) computer facility.

Two examples of the analysis of alloys are presented in this report to demonstrate the application of the computer program. In the first example, six standard reference materials are used to establish a calibration curve from which the composition of six unknown samples is calculated. In the second example, 23 iron-nickel-chromium alloys are used to determine the interelement correction coefficients for the determination of iron in these ternary alloys.

APPLICATION OF THE COMPUTER PROGRAM XRF4

Example 1.--Iron and Copper in Aluminum Alloys

The iron and copper content of a six aluminum disks (1-1/4 inches in diameter and 1 inch high) was to be determined by X-ray procedures. Six analyzed disks containing 0 to 0.76 weight-percent iron and 0 to 3 weight-percent copper were available as standard reference materials. The intensities of the iron and copper X-rays, and the iron and copper concentrations as listed in table 1, were submitted to the computer. The input format is shown in figure 1.

TABLE 1. - Iron and copper in aluminum alloys

Sample	Iron		Copper	
	Concentration, wt-pct	Intensity, cps	Concentration, wt-pct	Intensity, cps
1 A1..	0.00	371	0.00	406
2 A2..	.24	2,965	.05	554
3 A3..	.57	6,521	.15	843
4 A4..	.76	8,674	.74	2,437
5 A5..	.28	3,421	1.01	3,229
6 A6..	.34	3,944	3.00	7,845
7 S1..	-	2,890	-	487
8 S2..	-	3,376	-	2,184
9 S3..	-	3,067	-	570
10 S4..	-	1,069	-	519
11 S5..	-	1,133	-	752
12 S6..	-	4,231	-	594

```

3800 DATA "COPPER IN ALUMINUM ALLOYS"
3805 DATA 12,2,2
3810 DATA "CU","FE"
3820 DATA 1,1,406,554,843,2437,3229,7845
3825 DATA 487,2184,570,519,752,594
3830 DATA 4,1,"A1","A2","A3","A4","A5","A6"
3835 DATA "S1","S2","S3","S4","S5","S6"
3840 DATA 2,1,0,.05,.15,.74,1.01,3
3845 DATA 0,0,0,0,0,0
3850 DATA 2,2,0,.24,.57,.76,.28,.34
3855 DATA 0,0,0,0,0,0
3860 DATA 5,1,1,1,1,1,1,1,0,0,0,0,0,0
3870 DATA 1,2,371,2965,6521,8674,3421,3944
3875 DATA 2890,3376,3067,1069,1133,4231
4990 DATA 7,0

```

FIGURE 1. - Input format for example 1.

Input Information

Within the block of line numbers 2000-4980, the initial data are placed in temporary storage. A problem title, number of samples, number of components, identification of the components, and the intensity-composition data are entered into the program. For example:

```

line 3800 DATA "COPPER IN ALUMINUM ALLOYS"

3805 DATA 12,2,2

3810 DATA "CU" "FE"

```

The alphanumeric title of the problem is contained in the first data line, in this example, line 3800. The 3 numbers on the next line, 12, 2, and 2, define 12 samples and 2 components, and indicate that the initial calculations will be for component 2. The two components are next identified as "CU" and "FE" on line 3810. The complete listing of the input data for example 1 is shown in figure 1.

Subsequent input information consists of sets of 2 identifier codes plus a number of data points equal to the number of samples (12, in this example). The first code number, identified in the program as J1, defines the type of data to follow, either intensities, concentrations, sample names, or group identification. The second identifier code number, J2, defines the component with which the data are associated. The order of entry of the sets of data is not significant.

<u>J1 code number</u>	<u>Type of data</u>	<u>Program variable</u>
1	Peak intensity	Z(I,J)
2	Concentration	C(I,J)
3	Background intensity	V(I,J)
4	Sample name or number	S\$(I)
5	Group number	F(I)
7	End of data	

In the first example (fig. 1) the first 2 numbers in line 3820 preceded 12 values of peak intensity for component 1. The 2 code numbers in line 3830 preceded 12 alphanumeric sample names. Similarly, in line 3860, two code numbers were followed by group identification. The value 1 for group numbers is assigned to samples to be used as standards in the regression calculations. If no group distinctions are made, all samples are used in calculating the calibration curves. The code 7 in line 4990 signals the end of the data.

Program Operation

A number of options are available for treatment of the X-ray data, including different models, choice of standards, and choice of regression constraints. Therefore, a conversational mode of interaction with the computer is utilized for increased flexibility. After the computer stores the preliminary concentration, intensity, and descriptive information, the title and component descriptions are printed; then a statement is printed acknowledging that the correct number of datum values have been stored. In the first example, the printed output as illustrated in figure 2 is

COPPER IN ALUMINUM ALLOYS

IDENT J	COMPONENT
1	CU
2	FE

DATA IN....

A request from the computer is next printed, the computer pauses, and an operator response is required.

STEP = ?

The request STEP is encountered at several places in the program where differing choices might be useful, particularly printing out data, correcting

COPPER IN ALUMINUM ALLOYS

IDENT J	COMPONENT
1	CU
2	FE

DATA IN...
STEP = ? 1

MATRIX MODEL (M=0-6) ? 0

CONSTRAINTS(YES=1,NO=0) ? 0

2 COMPONENTS, 2 VARIABLES, 6 EQUATIONS

FE DATA		
COMPONENT	COEFFICIENT	CONTRIBUTION
BKGD	336.64	0.085
FE	1090.24E+01	1.000

SIGMA = 0.0058 LSQFIT = 0.999885

STEP = ? 2

COMPONENT J, FIRST I, LAST I = ? 2, 1, 12

SAMPLE	PCT CONC	PEAK INT	BKGD INT	CORR INT	CALC CONC
1 A1	0.000	371.0	0.0	371.00	0.003 STD
2 A2	0.240	2965.0	0.0	2965.00	0.241 STD
3 A3	0.570	6521.0	0.0	6521.00	0.567 STD
4 A4	0.760	8674.0	0.0	8674.00	0.765 STD
5 A5	0.280	3421.0	0.0	3421.00	0.283 STD
6 A6	0.340	3944.0	0.0	3944.00	0.331 STD
7 S1	0.000	2890.0	0.0	2890.00	0.234
8 S2	0.000	3376.0	0.0	3376.00	0.279
9 S3	0.000	3067.0	0.0	3067.00	0.250
10 S4	0.000	1069.0	0.0	1069.00	0.067
11 S5	0.000	1133.0	0.0	1133.00	0.073
12 S6	0.000	4231.0	0.0	4231.00	0.357

STEP = ? 6

STEP = ? 5

J2= ? 1

MATRIX MODEL (M=0-6) ? 0

CONSTRAINTS(YES=1,NO=0) ? 0

2 COMPONENTS, 2 VARIABLES, 6 EQUATIONS

CU DATA		
COMPONENT	COEFFICIENT	CONTRIBUTION
BKGD	509.18	0.249
CU	2476.55	1.000

SIGMA = 0.0585 LSQFIT = 0.998708

FIGURE 2. - Output for example 1.

STEP = ? 1

IF SAMPLE A6 WERE NOT USED AS A STANDARD,
THE STD DEV WOULD BE .007 AND THE FIT .999897
WOULD YOU LIKE TO ELIMINATE A STANDARD(YES=1,NO=0) ? 1
PRINT I.D. NO. ? 6

COMPONENT	CU DATA COEFFICIENT	CONTRIBUTION
BKGD	413.16	0.382
CU	2770.86	1.000

SIGMA = 0.0074 LSQFIT = 0.999897

STEP = ? 2

COMPONENT J, FIRST I, LAST I = ? 1, 1, 12

SAMPLE	PCT CONC	PEAK INT	BKGD INT	CORR INT	CALC CONC	
1 A1	0.000	406.0	0.0	406.00	-0.003	STD
2 A2	0.050	554.0	0.0	554.00	0.051	STD
3 A3	0.150	843.0	0.0	843.00	0.155	STD
4 A4	0.740	2437.0	0.0	2437.00	0.730	STD
5 A5	1.010	3229.0	0.0	3229.00	1.016	STD
6 A6	3.000	7845.0	0.0	7845.00	2.682	
7 S1	0.000	487.0	0.0	487.00	0.027	
8 S2	0.000	2184.0	0.0	2184.00	0.639	
9 S3	0.000	570.0	0.0	570.00	0.057	
10 S4	0.000	519.0	0.0	519.00	0.038	
11 S5	0.000	752.0	0.0	752.00	0.122	
12 S6	0.000	594.0	0.0	594.00	0.065	

STEP = ? 7

MATRIX MODEL (M=0-6) ? 4

CONSTRAINTS(YES=1,NO=0) ? 1

INPUT S,T (S=0 FIXED AT T,S=1 FREE,S=2 STORED)

BKGD = ? 0.406

A(CU) = ? 1.0

A(Fe) = ? 1.0

2 COMPONENTS, 2 VARIABLES, 5 EQUATIONS

COMPONENT	CU DATA COEFFICIENT	CONTRIBUTION
CU	2825.28	1.000
FE	3672.19E-05	0.017

SIGMA = 0.0049 LSQFIT = 0.999955

STEP = ? 9

FIGURE 2: - Output for example 1 (Con.).

mistakes, or changing options. There are 10 responses that direct the computer to various locations in the program, as follows:

<u>Response</u>	<u>Description</u>
1	Continue
2	Print out data
3	Recycle bypass
4	Print coefficients
5	Change component
6	Store calculated concentrations
7	Change model
8	Change constraints
9	End program
10	Change one sample

A more extensive description of each STEP option is given in appendix A. When in doubt, response 1 will allow the program to proceed normally. Other responses interrupt the program in the prescribed manner.

The request for which model to use for interelement correction is printed next on the computer output.

MATRIX MODEL (M = 0 - 6)?

The options are--

- 0 No interelement correction
- 1 Linear model
- 2 Self absorption
- 3 Lucas-Tooth
- 4 Lachance-Traill
- 5 Raspberry-Heinrich
- 6 Claisse-Quintin.

The next request that appears allows the operator to remove variables from the regression or to make corrections using coefficients that have been previously calculated.

CONSTRAINTS (YES = 1, NO = 0)?

The response 0 will cause the first six variables that have been defined, including a background or slope intercept, to be calculated. A response of 1 will list variables individually and require an operator response for each variable in the regression equation. Two responses for each variable are required, a code for S and a value for T. The value of T may be set at any real number. The choices for S are 0, 1, and 2. The code 0 removes the variable from the regression, but corrects the intensity by an amount determined by the value of T. A code 1 permits a value for the coefficient to be calculated by least squares fitting of the curve. A response S = 2 will use a stored value to correct the observed intensity. The following is printed only if constraints are to be used:

INPUT S, T (S = 0 FIXED AT T, S = 1 FREE, S = 2 STORED)

BKGD = ?

After the values of S and T are returned by the operator, the other variables appear on the computer output, each one requiring operator response:

A (CU) = ?

A (FE) = ?

The appropriate linear regression is then performed. The values of the calculated coefficients, the standard deviation, and the goodness of fit are printed out. Application of the use of constraints is given in appendix D in the description of the models.

The computer will next automatically calculate the best fit to the curve when each of the standards in turn is eliminated from the fit. The curve indicating the best statistical fit with one less standard is identified, and the eliminated standard is flagged. The request then appears on the output: WOULD YOU LIKE TO ELIMINATE A STANDARD (YES = 1, NO = 0)?

If the response is 0, the STEP = ? request appears and the program is ended unless further calculations using this set of data are needed, such as changing the model or the constraints or changing the dependent variable.

The printed output for the first example is shown in figure 2. A simple regression without matrix correction of iron intensity on concentration was the result of the responses 0 and 0 to the request for selection of matrix model and constraints. An intercept of 336.64 cps and a slope of 10,902.4 cps/pct Fe were calculated. The standard deviation about the regression line was calculated to be 0.0058 weight-percent iron, well within the precision of the known iron concentrations. The relevant information for the iron determinations,

including the calculated concentrations of all the samples, was printed out. The calculated concentrations of the unknown samples were stored in the computer for future calculation by means of a response of 6 to the request for STEP = ? The numerical response 5 to the STEP request was followed by the request J2 = ? which was asking for the identification number of the new component to be used to establish a new calibration curve. In this example, copper was identified as component 1. For the copper intensity-concentration data, model 0 with no constraints generated an intercept of 509.18 cps and a slope of 2,476.55 cps/pct Cu. A standard deviation of 0.0585 percent Cu was considerably larger than that which would be expected from statistical counting error alone. The computer calculated that if sample A6 were not used as a standard, the statistical fit would be improved by almost an order of magnitude. Sample A6 contained 3.00 percent copper, significantly higher than the copper content expected to be found in the unknown samples, and was therefore eliminated from the regression. The new intercept of 413.16 cps was acceptably close to the value of 406 expected from measurement of the blank sample A1. The information for the copper determinations was then printed out. Since the concentration data were only presented to two decimal places, further calculation was not warranted.

To illustrate the use of interelement corrections and constraints, the effect of iron in the measurement of copper in aluminum was calculated, using the Lachance-Traill model and anchoring the intercept at 406 cps. The value of 0.0049 for sigma indicated some improvement in the statistics, but the value of 0.017 for the contribution of iron indicated that iron has little effect on the copper intensities, at least at the levels encountered in these samples. The CONTRIBUTION value in this program is included as an aid to the analyst. It is defined as

$$\sum_{j=1}^n (A_j * X_{1j}) / (A_k * X_{1k}),$$

where A_k and A_j are the coefficients for components j and k . The value of K is always the identification number of the dependent variable; that is, the element for which the calibration curve is being established. The CONTRIBUTION term serves a function comparable to an F-test.

Example 2.--Iron-Nickel-Chromium Alloys

Some of the data presented in Rasberry and Heinrich's paper⁴ was submitted to the matrix correction procedures. The calibration curves for iron were determined using 23 standard iron-nickel-chromium alloys. The input data are shown in figure 3. The best least squares line with no interelement compensation gave a standard deviation of 13.94 percent iron. The standard deviation and goodness-of-fit for each of the models are shown in table 2.

⁴Rasberry, S. D., and K. F. J. Heinrich. Calibration for Interelement Effects in X-Ray Fluorescence. Anal. Chem., v. 46, 1974, pp. 81-89.

```

3800 DATA "R-H DATA ANAL.CHEM.46,P86(1974)"
3802 DATA 23,3,1
3804 DATA "FE","NI","CR"
3806 DATA 2,1,4.62,6.59,10.18,22.63,30.67,34.31,51.63,15,95.49
3808 DATA 96.27,93.72,87.66,80.8,74.77,67.86,63.22
3810 DATA 68.38,69.45,52.8,59.19,71.59,15.01,1.4
3812 DATA 2,2,95.16,93.22,89.64,77.11
3814 DATA 69.31,65.52,48.2,35.99,3.29
3816 DATA 0,0,0,0,0,0,0
3818 DATA 4.98,9.96,19.27,20.02,8.29,64.29,72.6
3820 DATA 2,3,0,0,0,0,0,0,0,0
3822 DATA 3.53,6.08,12.14,19,25.03,31.94,36.58
3824 DATA 25.25,19.88,26.96,19.88,18.79,16.88,20.3
3826 DATA 1,1,789,1104,1621,3172,4007
3828 DATA 4373,5907,6958,9659
3830 DATA 8970,8270,6974,5739,4748,4048,3579
3832 DATA 4511,4971,3529,4343,5298,1460,125
3834 DATA 1,2,8782,8321,7595,5483
3836 DATA 4515,4073,2553,1720,125
3838 DATA 0,0,0,0,0,0,0
3840 DATA 203,416,821,898,343,4367,5630
3842 DATA 1,3,0,0,0,0,0,0,0,0
3844 DATA 617,1004,1817,2587,3326,4023,4476
3846 DATA 3258,2651,3311,2582,2536,2072,2263
3848 DATA 4,1,"971","972","974","983"
3850 DATA "986","987","1159","126B","809B"
3852 DATA "4061","4062","4065","4173"
3854 DATA "4181","4183","4184"
3856 DATA "5074","5181","5324","5321"
3858 DATA "7271","161","1189"

```

FIGURE 3. - Input data for example 2.

TABLE 2. - Comparison of results from six procedures using
Raspberry-Heinrich Fe-Ni-Cr

Model	Interelement method	Number of variables	Standard deviation, percent Fe	Goodness-of fit
0....	None.....	1	13.94	0.9504
1....	Linear model.....	3	4.68	.9949
2....	Self absorption....	4	5.11	.9942
3....	Lucas-Tooth.....	3	4.82	.9946
4....	Lachance-Traill....	3	.95	.9998
5....	Raspberry-Heinrich..	3	.67	.9999
6....	Claisse-Quintin....	6	.59	.9999

Not surprisingly, the Raspberry-Heinrich model gave a good fit with only 3 free parameters; the Claisse-Quintin procedure, with 6 free parameters, yielded a slightly better fit for this set of data.

In figure 4, the first calculation of the iron intensity-concentration relationship was made with no constraints and no interelement corrections.

R-H DATA ANAL.CHEM.46,P86(1974)

IDENT J	COMPONENT
1	FE
2	NI
3	CR

DATA IN...

STEP = ? 1

MATRIX MODEL (M=0-6) ? 0

CONSTRAINTS(YES=1,NO=0) ? 0

3 COMPONENTS, 2 VARIABLES, 23 EQUATIONS

FE DATA		
COMPONENT	COEFFICIENT	CONTRIBUTION
BKGD	605.79	0.154
FE	73.91	1.000

SIGMA = 15.3426 LSQFIT = 0.942590

STEP = ? 7

FIGURE 4. - Output for example 2, Fe-Ni-Cr alloys.

MATRIX MODEL (M=0-6) ? 4

CONSTRAINTS(YES=1,NO=0) ? 1

INPUT S,T (S=0 FIXED AT T,S=1 FREE,S=2 STORED)

BKGD = ? 0,0

A(FE) = ? 1,0

A(NI) = ? 1,0

A(CR) = ? 1,0

3 COMPONENTS, 3 VARIABLES, 23 EQUATIONS

COMPONENT	FE DATA COEFFICIENT	CONTRIBUTION
FE	99.33	1.000
NI	-340.13E-05	0.058
CR	2086.21E-05	0.202

SIGMA = 0.9460 LSQFIT = 0.999792

STEP = ? 1

IF SAMPLE 4181 WERE NOT USED AS A STANDARD,
THE STD DEV WOULD BE .837 AND THE FIT .999835
WOULD YOU LIKE TO ELIMINATE A STANDARD(YES=1,NO=0) ? 0

STEP = ? 7

MATRIX MODEL (M=0-6) ? 5

CONSTRAINTS(YES=1,NO=0) ? 1

INPUT S,T (S=0 FIXED AT T,S=1 FREE,S=2 STORED)

BKGD = ? 0,0

A(FE) = ? 1,0

B(FE) = ? 0,0

A(NI) = ? 0,0

B(NI) = ? 1,0

A(CR) = ? 1,0

B(CR) = ? 0,0

3 COMPONENTS, 3 VARIABLES, 23 EQUATIONS

COMPONENT	FE DATA COEFFICIENT	CONTRIBUTION
FE	99.84	1.000
B2	-0.45	0.057
CR	2108.73E-05	0.203

SIGMA = 0.6696 LSQFIT = 0.999896

STEP = ? 1

IF SAMPLE 4181 WERE NOT USED AS A STANDARD,
THE STD DEV WOULD BE .453 AND THE FIT .999951
WOULD YOU LIKE TO ELIMINATE A STANDARD(YES=1,NO=0) ? 0

STEP = ? 1

FIGURE 4: - Output for example 2, Fe-Ni-Cr alloys (Con.).

All 23 samples were utilized as standards to calculate the interelement correction coefficients. These iron-nickel-chromium alloys manifest significant interelement effects, as indicated from the large error in the calibration curve corresponding to 15.3426 percent iron. This value is different from the value in the table where background correction was used. Late in the calculation, as shown on the second page of figure 4, matrix model 4 was requested with the intercept constrained to be zero. The reported intensity data had been background corrected, and the calibration curve would, therefore, be expected to pass through the origin of the intensity-concentration plot.

The value of 0.9460 percent iron is a significant improvement in the standard deviation for the regression line when Lachance-Traill interelement corrections are applied.

The Raspberry-Heinrich correction, model 5, was next applied with more improvement. In both interelement correction procedures, the same sample, 4181, was identified as the sample whose removal would most improve the calibration curve. The degree of improvement was presented in the computer printout.

CONCLUSIONS

The computer program XRF4 has been formulated for use by analytical chemists with minimal computer training. Approximately 9,000 words of computer storage are required, a large portion of this being used to format the output for ease in data handling. The calculation algorithms are reasonably efficient. Each of the examples in this report cost less than a dollar of computer time to run. The applications of the various models for interelement correction been described elsewhere, as has the testing of the regression algorithms.⁵ A listing of the program is presented in appendix E of this report.

⁵Third work cited in footnote 2.

APPENDIX.--STEP OPTIONS

<u>STEP options</u>	<u>Descriptions of STEP option</u>
1	Continue with program. When in doubt use this value.
2	Print out all information for one component; that is, sample number and name, percent concentration, peak intensity, background intensity, peak minus background, and calculated concentration from standard curve. Unknown values are reported as zero. When option 2 is chosen, the request COMPONENT J, FIRST I, LAST = ? appears on the computer printout. Three integer values are required: the identification number of the component, and the identification numbers of the first and last samples in a sequence for which the printout is desired. A value of 0 for the component number is a special case, which causes the concentration values for all components to be printed out in a table.
3	Recycle bypass. An important safeguard for the analyst using this program is that the data are automatically tested for improvement in the calibration curve when each of the standards in turn is eliminated from the fit. This makes it possible to locate errors in the data that would most certainly go unnoticed in other available programs designed for the reduction of X-ray data. The recycling of all the data can be time-consuming, however. The capability of crippling this option is therefore included in the procedure. This bypass would be used following the calculation of SIGMA and LSQFIT.
4	Print out the array of regression coefficients including those under constraint. The program normally prints only the coefficients calculated in the previous regression.
5	Change the component providing the dependent variable, that is, the component identified as J2. The request J2 = ? will appear on the computer printout.
6	Store calculated concentrations of samples for future inter-element corrections. The values are stored for all samples not identified as standards.
7	Change model for interelement correction. This command transfers to the appropriate location in the program.
8	Change constraints. This command retains the model but allows the constraints to be changed. The same samples that had been identified as standards will be identified as standards when the model or constraints are changed.

STEP optionsDescriptions of STEP option

- 9 End program.
- 10 Change the values assigned to one sample. This option is useful for correcting input typing errors to eliminate certain standards from the regression.

Other samples can be included in the regression by changing the group identification to 1 with the use of this option. Since the program returns to the STEP request each time, several samples can be changed. It is usually more convenient to change a DATA line in the input and rerun the program, but occasionally a lot of data are stored from previous calibration curves and it becomes more convenient to change the group numbers one at a time. When this STEP option is requested the line appears: I, J = ?

The response is the sample number and component number. Then the line appears: F(I,J), C(I,J), Z(I,J), V(I,J) = ? The response for sample I, component J is four values, for group number, concentration, peak intensity, and background intensity. Any unknown values are entered as zero.

APPENDIX B.--PROGRAM MODIFICATIONS

Dimensions.--The computer program XRF4 is dimensioned to handle a total of 25 samples and standards. For special problems it may be convenient to process a greater number, depending on the available computer core. At College Park as many as 77 samples with 6 components have been analyzed in 1 pass. The computer program is simply redimensioned in lines 125 and 130 to accommodate the number of samples required. The value 25 is replaced with the appropriate number in each of the arrays. The maximum number of components is six and cannot be increased. The program has been tested for the use of six variables (components); the calculation of more variables may introduce error in the solution of simultaneous equations.

Sample names.--Lines 205 through 230 contain the capability of changing the numerical value of the sample to an alphanumeric character for identification of the sample. This sample name is overridden when sample identification is entered into the program as input data, but it is useful when such input data is not included. The CHANGE command in line 230 is not available in all BASIC compilers, and this block of lines can be omitted from the program.

APPENDIX C.--VARIABLES FOR XRF4

Simple variables

A	Option for constraints
A0	Background option code
A1	Value of intercept or background
C	Loop counter, columns
G1	Number of standard samples
H1	Sum of concentrations
I	Loop counter, samples
I1	Number of samples
I2	Counter, first sample number
I3	Counter, last sample number
J	Loop counter, components
J1	Number of components
J2	Component providing dependent variable
J4	Component in regression
K	Loop counter, variables
K1	Number of variables in regression
M	Model number
R	Loop counter, rows
S	Input for branching option
S1	Partial sum
S4	Partial sum
T	Value of coefficient
T1	Temporary storage

X1 Error fit
X2 Standard deviation
X3 Standard deviation
X7 Error fit
X8 Error fit
X9 Standard deviation
Z1 Counter, background
Z2 Counter, variables
Z3 Standard deviation
Z4 Error fit
Z5 Counter, unassigned

Arrays

A(K) Coefficients
B(R,C) Partial sums
C(K,J) Concentrations
D(L) Calculated concentrations
F(I) Group number
G(O) Change subroutine storage
H(J) Partial sums for matrix inversion
S(J) Code for regression option
T(J) Coefficients
V(I,J) Background intensities
X(I,J) Inversion matrix
Y(I) Corrected intensities
Z(I,J) Intensities for J components

String variables

A\$ Problem name, standard identifier

S\$ Sample name

String arrays

B\$(J) Component names

C\$(J) Component names, ordered

J\$(J) Component names, original

S\$(I) Sample name

APPENDIX D.--MODELS FOR INTERELEMENT CORRECTION

The objective of X-ray analysis is to determine composition of an unknown sample from observation of the distribution of X-rays from the sample. It is, therefore, usually convenient to establish calibration plots where intensity of a characteristic X-ray line is plotted against the concentration of one element in a multielement matrix. If the concentration axis is the x axis, then the y axis becomes the observed intensity corrected for interelement effects. The following descriptions of the models are presented using the notation of the computer program and data from example 2; that is, the determination of iron in iron-nickel-chromium alloys. The general forms of the equations have been described elsewhere.¹

Model 0.--No Interelement Correction

The simplest correlation between intensity and concentration that includes a background correction is expressed by the simple linear regression equation

$$Z(I,1) = A1 + A(1)*C(I,1). \quad (D-1)$$

iron

This equation often gives a good first approximation for the concentration of unknown samples, and is used to determine if interelement corrections are warranted for a given set of samples and standard reference materials.

Model 1.--Linear Model

The equation

$$Z(I,1) = A1 + A(1)*C(I,1) + A(2)*C(I,2) + A(3)*C(I,3) \quad (D-2)$$

iron nickel chromium

is a first-order linear correction of X-ray intensities for interelement effects of the various elements in an alloy. Of the several popular matrix correction models, this linear regression equation is not a particularly good approximation of Sherman's equations for correlating X-ray intensities to composition. A simple linear regression procedure, however, is readily available in most computer facilities and required minimal pretreatment of data. It is therefore often still used for interelement corrections. Of more recent application is its capability in energy-dispersive analysis for treatment of overlapping spectra and other spectral interferences, as well as compensation for absorption-enhancement effects.

¹Marr, H. E. Six Models for Interelement Correction in X-Ray Analysis. Advances in X-Ray Analysis, v. 19, 1975, pp. 167-180.

If no constraints are imposed, values for A_1 , $A(1)$, $A(2)$, and $A(3)$ would be calculated in the program by least squares methods using measured iron intensities, $Z(I,1)$, and known concentrations of iron $C(I,1)$, nickel $C(I,2)$, and chromium $C(I,3)$. If the intensity data had been previously corrected for background, the value of A_1 would be constrained to be zero. If the inter-element correction coefficients for other elements were known from previous measurements, then these values could be entered into the program. For example, if, under a given set of measurement conditions, the value of the correction coefficient for nickel on iron intensities were 12, the response to the computer requesting constraints would be values for S and T of 0 and 12:

$$A(NI) = ? 0, 12.$$

If this were the only constraint, the variables A_1 , $A(1)$, and $A(3)$ would be calculated, $A(2)$ being the same as $A(NI)$. The observed intensity of iron would be automatically corrected for nickel content. If background intensities were measured elsewhere in the spectrum, the response for BKGD would have been

$$BKGD = ? 2, 0.$$

The value 0 is not significant, since the value for T is taken from the stored data and the original intensity of each sample is corrected by the value of T . At present, the response $S = 2$ is confined to the BKGD variable, and the array $V(I,J)$ contains the intensities to be subtracted as background intensities.

Model 2.--Self-Absorption Correction Procedure

In samples where the variation in the element being determined is great enough to effect a change in the density or average mass absorption of the matrix, a deviation from the line may be noted in a calibration curve. This behavior is not uncommon in binary systems or in samples where a heavy (high atomic number) element is being determined in a lighter (lower average atomic number) matrix.

An additional term containing a function of the element being determined is applied to the regression equation:

$$Z(I,1) = A_1 + \underset{\text{iron}}{A(1)*C(I,1)} + \underset{\text{nickel}}{A(2)*C(I,2)} + \underset{\text{chromium}}{A(3)*C(I,3)} + \underset{\text{iron}}{A(4)*C(I,1)}^2 \quad (D-3)$$

Several models utilize a term requiring a value for the concentration of the element being determined, necessitating first approximations of the unknown composition and iterative computations. A simple linear regression with no interelement compensation serves as a first approximation.

Model 3.--Lucas-Tooth Procedure

The fact that interelement corrections require a knowledge of the concentrations of the other elements in the matrix is a source of some inconvenience

when dealing with samples of unknown composition. This difficulty can be handled by substituting the observed intensities of the characteristic X-ray lines of the other elements as suggested by Lucas-Tooth. The simplest Lucas-Tooth type model is the equation

$$Z(I,1) = A1 + A(1)*C(I,1) + A(2)*Z(I,2) + A(3)*Z(I,3). \quad (D-4)$$

iron nickel chromium

This particular model is useful for the reduction of data obtained in energy-dispersive systems and multielement wavelength spectrometers, because the intensities of other elements are readily available.

The Lucas-Tooth model in the program is not a good representation of the procedure for interelement correction originally reported by Lucas-Tooth. The original method resembled the Lachance-Traill procedure, replacing known concentrations in the equation with measured intensities. The Lucas-Tooth model can be changed in the program by changing line 840 to read

$$840 \text{ LET } X(I,K) = -Y(I)*Z(I,J).$$

This model will give a good correction for absorption effects, but it will not be as effective for correcting for overlapping spectra.

Model 4.--Lachance-Traill Procedure

The intensity-concentration relation described by Lachance and Traill is expressed by the equation

$$Z(I,1)*(1 + A(2)*C(I,2) + A(3)*C(I,3)) = A1 + A(1)*C(I,1). \quad (D-5)$$

nickel chromium iron

This equation is the first model in a series of increasing complexity where the correction term is a factor by which the observed intensity is multiplied. These equations are much better approximations of Sherman's equations for correlating the X-ray intensity to composition than the first three linear regression models. In the Lachance-Traill procedure the enhancement of intensity of one element due to secondary fluorescence from another element is conceptually described as a negative absorption. The coefficients derived from fitting these equations are popularly called alpha constants.

Model 5.--Rasberry-Heinrich Procedure

The model proposed by Rasberry and Heinrich is represented by the equation

$$Z(I,1)*(1 + \sum_{J=2}^n A(J)*C(I,J) + \sum_{J=2}^n B(J)*C(I,J)/(100 + C(I,1)))$$

$$= A1 + A(1)*C(I,1). \quad (D-6)$$

This model is designed to separate enhancement effects from absorption effects. The equation as presented would be expected to improve on the Lachance-Traill procedure because twice as many variables are incorporated in the curve fitting. Because of the similarity of the A and B terms in many sets of samples where the element being determined is in low concentration, the solution of the simultaneous equations to which the data is reduced would be impractical. To avoid this problem and to reduce the number of required standards, Rasberry and Heinrich suggested that only one of the terms would be used for each element, and that this could be predicted from tables of absorption edges and X-ray emission lines.

In the iron-nickel-chromium alloys, chromium would be expected to absorb the iron radiation and the A coefficient would be included in the regression. Nickel, whose X-ray emission lines are above the absorption edge of iron, would be expected to enhance the emission of iron X-rays, and the B coefficient would therefore be more appropriately included in the regression. The Rasberry-Heinrich equation for example 2 is expressed as follows:

$$Z(i,1) * (1 + A(3) * C(I,3) + B(2) * C(I,2) / (100 + C(I,1))) \\ = A1 + A(1) * C(I,1). \quad (D-7)$$

In the computer program constraints are necessary to repress the determination of the other coefficients. The series of conversational responses to the computer for this example is shown on the second page of figure 4 and in the following list:

```
CONSTRAINTS (YES = 1, NO = )? 1

INPUT S, T(S = 0 FIXED AT T, S = 1 FREE, S = 2 STORED)

BKGD = ? 0, 0

A(FE) = ? 1, 0

B(FE) = ? 0, 0

A(NI) = ? 0, 0

B(NI) = ? 1, 0

A(CR) = ? 1, 0

B(CR) = ? 0, 0
```

In this example, the background was fixed at 0, as were the contributions of the A coefficient of nickel and the B coefficients for iron and chromium. The other variables were free to be determined by linear regression least squares procedures. The values of the B coefficients reported in XRF4 will be a factor of 100 greater than those reported by Rasberry and Heinrich, because concentrations in XRF4 are percent values, not weight fractions as used in the original paper.

Model 6.--Claisse-Quintin Procedure

A generalization of the Lachance-Traill method for interelement corrections that is very effective is the Claisse-Quintin procedure. As noted by Rasberry and Heinrich and applied to their own data, the Claisse-Quintin method provides a better fit of the data than the Rasberry-Heinrich procedure. The limitation to the method is the requirement for several additional variables in the fit, necessitating additional standards. Some of the cross-product terms are more significant than others. The number of required standards can be reduced to a manageable level by judicious selection of the variables to be included in the fitting procedure. The equation describing the Claisse-Quintin procedure is:

$$\begin{aligned}
 Z(I,1) * (1 + \sum_{J=2}^n A(J) * C(I,J) + \sum_{J=2}^n \sum_{K=2}^n B(J,K) * C(I,J) * C(I,K)) \\
 = A_1 + A(1) * C(I,1). \qquad \qquad \qquad (D-8)
 \end{aligned}$$

APPENDIX E.--LISTING OF XRF4

```

100 REM XRF4  9-29-75  H.E.MARR
105 REM PROGRAM FOR CORRELATING X-RAY INTENSITIES TO
110 REM CONCENTRATIONS INCLUDING INTERELEMENT CORRECTIONS.
115 DIM A(8),B(7,9),B$(8),C$(8),J$(12)
120 DIM G(3),H(8),S(12),T(12)
125 DIM C(25,6),D(25),F(25),S$(25),V(25,6)
130 DIM X(25,8),Y(25),Z(25,6)
135 FOR J= 7 TO 12
140 READ J$(J)
145 NEXT J
150 DATA "B1","B2","B3","B4","B5","B6"
155 REM *** INPUT DATA ***
160 READ A$,I1,J1,J2
165 PRINT A$
170 PRINT
175 PRINT "IDENT J      COMPONENT"
180 LET G1=I1
185 FOR J = 1 TO J1
190 READ J$(J)
195 PRINT J,J$(J)
200 NEXT J
205 LET G(0)=2
210 FOR I = 1 TO I1
215 LET F(I) = 1
220 LET G(2)=48+I-10*INT(I/10)
225 LET G(1)=48+INT(I/10)
230 CHANGE G TO S$(I)
235 NEXT I
240 PRINT
245 REM INPUT A1,J FOR I,C,BKGD DATA
250 READ A1,J
251 PRINT A1;J,
255 ON A1 GOTO 260,280,300,320,340,370,370
260 FOR I = 1 TO I1
265 READ Z(I,J)
270 NEXT I
275 GO TO 250
280 FOR I = 1 TO I1
285 READ C(I,J)
290 NEXT I
295 GO TO 250
300 FOR I = 1 TO I1
305 READ V(I,J)
310 NEXT I
315 GO TO 250
320 FOR I = 1 TO I1
325 READ S$(I)
330 NEXT I
335 GO TO 250

```

```

340 FOR I = 1 TO I1
345 READ F(I)
350 IF F(I)=1 THEN 360
355 LET G1=G1-1
360 NEXT I
365 GO TO 250
370 PRINT
375 PRINT "DATA IN..."
380 GOSUB 1710
385 PRINT
390 PRINT "MATRIX MODEL (M=0-6)";
395 INPUT M
400 PRINT
405 REM MODIFICATION FOR CLAISSE-QUINTIN
410 IF M<6 THEN 490
415 LET M=4
420 IF J1>3 THEN 500
425 LET K= J1
430 FOR J= 1 TO J1
435 IF J=J2 THEN 480
440 FOR R= 1 TO J
445 IF R= J2 THEN 475
450 LET K=K+1
455 FOR I= 1 TO I1
460 LET C(I,K)=C(I,J)*C(I,R)
465 NEXT I
470 LET J$(K)=J$(J+R+5)
475 NEXT R
480 NEXT J
485 LET J1=J1*J1-J1
490 IF M>0 THEN 505
495 LET M= 8
500 REM CHECK FOR REGRESSION CONSTRAINTS
505 PRINT "CONSTRAINTS (YES=1,NO=0)";
510 INPUT A
515 REM A = 0,1 (YES =1,NO =0)
520 IF A = 1 THEN 560
525 FOR J=1 TO J1
530 LET S(J)=1
535 LET S(J+6)=1
540 NEXT J
545 LET A0=1
550 LET A1=0
555 GO TO 625
560 PRINT "INPUT S,T (S=0 FIXED AT T,S=1 FREE,S=2 STORED)
565 PRINT "BKGD =";
570 INPUT A0,A1
575 LET S(J2)=1
580 IF M=8 THEN 625
585 REM A0 = 0,1,2 FOR KNOWN BKGD,FREE TO VARY,OR V ARRAY.
590 FOR J = 1 TO J1

```

```

595 PRINT "A(";J$(J);") =";
600 INPUT S(J),T(J)
605 IF M<5 THEN 620
610 PRINT "B(":J$(J);") =";
615 INPUT S(J+6),T(J+6)
620 NEXT J
625 PRINT
630 REM CORRECT FOR BKGD AND FILL X(I,1) ARRAY
635 MAT X=ZER
640 LET Z5=0
645 LET Z1=A0*(2-A0)
650 LET K=Z1+1
655 LET Z2=S(J2)*(2-S(J2))
660 FOR I=1 TO I1
665 LET X(I,1)=1
670 LET X(I,K)=C(I,J2)
675 IF Z2=1 THEN 685
680 LET X(I,8)=C(I,J2)*T(J2)
685 NEXT I
690 LET C$(1)="BKGD"
695 LET C$(K)=J$(J2)
700 FOR I = 1 TO I1
705 IF A0<2 THEN 715
710 LET A1=V(I,J2)
715 LET Y(I)=Z(I,J2)-A1
720 NEXT I
725 REM FILL D(I)
730 LET K1=K
735 GOSUB 1260
740 IF M=8 THEN 985
745 LET Z3=X2
750 LET Z4=X1
755 LET K=Z1+Z2
760 IF M<>2 THEN 800
765 LET K=K+1
770 LET Z5=1
775 FOR I= 1 TO I1
780 LET X(I,K)=D(I)*D(I)
785 NEXT I
790 LET C$(K)="X+2"
795 REM FILL X ARRAYS
800 FOR J=1 TO J1
805 LET J4=J
810 IF J4=J2 THEN 965
815 LET K=K+1
820 FOR I = 1 TO I1
825 ON M GOTO 830,830,840,850,850,860
830 LET X(I,K)=C(I,J)
835 GO TO 880
840 LET X(I,K)=Z(I,J)
845 GO TO 880

```

```

850 LET X(I,K)=-Y(I)*C(I,J)
855 GO TO 880
860 IF F(I)=1 THEN 875
865 LET X(I,K)=-C(I,J)*Y(I)/(100+D(I))
870 GO TO 880
875 LET X(I,K)=-C(I,J)*Y(I)/(100+C(I,J2))
880 NEXT I
885 LET C$(K)=J$(J4)
890 REM CHECK FOR KNOWN VALUES
895 REM
900 IF S(J4)=1 THEN 925
905 FOR I = 1 TO I1
910 LET X(I,8)=X(I,8)+X(I,K)*T(J4)
915 NEXT I
920 LET K =K-1
925 IF K<7 THEN 940
930 LET K=6
935 GO TO 970
940 ON M GO TO 965,965,965,965,945,960
945 LET M=6
950 LET J4=J4+6
955 GO TO 815
960 LET M=5
965 NEXT J
970 FOR I=1 TO I1
975 LET Y(I)=Y(I)-X(I,8)
980 NEXT I
985 PRINT J1;" COMPONENTS, ";K; " VARIABLES, ";G1;" EQUATIONS"
990 LET K1=K
995 GOSUB 1260
1000 IF G1>2*K1 THEN 1015
1005 PRINT " *** CAUTION, ONLY";G1;" STANDARDS, ";K1;" VARIABLES"
1010 PRINT
1015 PRINT" ",J$(JF);" DATA"
1020 PRINT "COMPONENT","COEFFICIENT","CONTRIBUTION"
1025 FOR K=1 TO K1
1030 LET T=ABS(A(K)*H(K)/(H1*T(J2)))
1035 IF ABS(A(K))>9999 THEN 1060
1040 IF ABS(A(K))<.1 THEN 1060
1045 PRINT USING 1050,C$(K),A(K),T
1050: 'LLLL      #####.##      ##.###
1055 GO TO 1070
1060 PRINT USING 1065,C$(K),A(K),T
1065: 'LLLL      #####.## ↑↑↑↑      ##.###
1070 NEXT K
1075 PRINT
1080 PRINT USING 1085,X2,X1
1085: SIGMA = ##.### LSQFIT = #.#####
1090 PRINT
1095 GOSUB 1710
1100 REM

```



```

1105 REM RECYCLE DATA ELIMINATING ONE STD
1110 LET X7=0
1115 LET X9=X2
1120 FOR S= 1 TO I1
1125 IF F(S)= 0 THEN 1170
1130 LET F(S)=0
1135 GOSUB 1260
1140 LET F(S)=1
1145 IF X2>X9 THEN 1170
1150 LET X$=S$(S)
1155 LET X9=X2
1160 LET X8=X1
1165 LET X7=1
1170 NEXT S
1175 IF X7<1 THEN 1200
1180 PRINT
1185 LET X9=INT(1000*X9+.5)/1000
1190 PRINT "IF SAMPLE ";X$;" WERE NOT USED AS A STANDARD,"
1195 PRINT"THE STD DEV WOULD BE";X9;" AND THE FIT";X8
1200 PRINT "WOULD YOU LIKE TO ELIMINATE A STANDARD";
1205 PRINT "(YES=1,NO=0)";
1210 INPUT T
1215 IF T = 0 THEN 1240
1220 PRINT"PRINT I.D. NO.";
1225 INPUT I
1230 LET F(I)=0
1235 GO TO 995
1240 PRINT
1245 GOSUB 1710
1250 GO TO 1970
1255 REM MATRIX INVERSION, SOLVE SIMUL. EQNS.
1260 LET G1=S1=H1=0
1265 MAT B = ZER
1270 MAT H = ZER
1275 FOR I = 1 TO I1
1280 REM TEST FOR STDs
1285 IF F(I) = 0 THEN 1340
1290 LET H1=H1+C(I,J2)
1295 LET G1 = G1 + 1
1300 FOR R= 1 TO K1
1305 FOR C = 1 TO R
1310 LET B(R,C) = B(R,C)+X(I,R)*X(I,C)
1315 LET B(C,R) = B(R,C)
1320 NEXT C
1325 LET B(R,K1+1)=B(R,K1+1)+Y(I)*X(I,R)
1330 LET H(R) = H(R)+X(I,R)
1335 NEXT R
1340 NEXT I
1345 IF G1>K1-1 THEN 1360
1350 PRINT G1;" EQUATIONS,";K1;" VARIABLES."
1355 GOSUB 1710

```

```

1360 FOR R= 1 TO K1
1365 FOR C= 1 TO K1
1370 IF B(R,C) = 0 THEN 1405
1375 FOR J= 1 TO K1+1
1380 LET T = B(R,J)
1385 LET B(R,J) = B(C,J)
1390 LET B(C,J) = T
1395 NEXT J
1400 GO TO 1415
1405 NEXT C
1410 GO TO 1470
1415 LET T = B(R,R)
1420 FOR K= 1 TO K1+1
1425 LET B(R,K) = B(R,K)/T
1430 NEXT K
1435 FOR J= 1 TO K1
1440 IF J = R THEN 1465
1445 LET T1=B(J,R)
1450 FOR T= 1 TO K1+1
1455 LET B(J,T) = B(J,T) -T1*B(R,T)
1460 NEXT T
1465 NEXT J
1470 NEXT R
1475 REM SORT COEFFICIENTS
1480 FOR K=1 TO K1
1485 LET A(K)=B(K,K1+1)
1490 NEXT K
1495 IF Z1=0 THEN 1505
1500 LET A1=A(1)
1505 IF Z2=0 THEN 1515
1510 LET T(J2)=A(Z1+1)
1515 LET K=Z1+Z2
1520 IF M= 8 THEN 1605
1525 IF M<> 2 THEN 1535
1530 LET K=K+1
1535 FOR J=1 TO J1
1540 LET J4=J
1545 IF J4=J2 THEN 1595
1550 IF S(J4)=0 THEN 1570
1555 LET K=K+1
1560 IF K>6 THEN 1605
1565 LET T(J4)=A(K)
1570 ON M GOTO 1595,1595,1595,1595,1575,1590
1575 LET M=6
1580 LET J4=J4+6
1585 GO TO 1545
1590 LET M= 5
1595 NEXT J
1600 REM CALCULATE STD DEV, LSQFIT
1605 LET S1=S4=0
1610 FOR I= 1 TO I1

```

```

1615 LET Y1=Y(I)
1620 FOR K= 1 TO K1
1625 LET Y1=Y1-A(K)*X(I,K)
1630 NEXT K
1635 IF T(J2)=0 THEN 1700
1640 LET T= Y1/T(J2)
1645 IF F(I)=0 THEN 1660
1650 LET S1=S1+T*T
1655 LET S4=S4+C(I,J2)2
1660 LET D(I)=T+C(I,J2)
1665 NEXT I
1670 LET X1=1
1675 LET X2 = 0
1680 IF G1=K1 THEN 1695
1685 LET X1 = 1 - S1/S4
1690 LET X2=SQR(S1/(G1-K1))
1695 RETURN
1700 PRINT "T(J2)= 0"
1705 REM OPTIONS FOR IO. OR CHANGING CONDITIONS
1710 PRINT"STEP =";
1715 INPUT S
1720 ON S GOTO 1965,1725,1200,1805,1845,1860,390,505,1970,1885
1725 PRINT"COMPONENT J,FIRST I, LAST I =";
1730 INPUT J,12,13
1735 IF J<1 THEN 1910
1740 PRINT USING 1745
1745: SAMPLE PCT CONC PEAK INT BKGD INT CORR INT CALC CONC
1750 FOR I = 12 TO 13
1755 LET A$=" "
1760 IF F(I)=0 THEN 1770
1765 LET A$="STD"
1770 IF J = J2 THEN 1790
1775 PRINT USING 1780,I,S$(I),C(I,J),Z(I,J),V(I,J)
1780: ### 'LLLL ###.### #####.###.###.###.###.###.### 'LLL
1785 GO TO 1795
1790 PRINT USING 1780,I,S$(I),C(I,J),Z(I,J),V(I,J),Y(I),D(I),A$
1795 NEXT I
1800 GO TO 1710
1805 PRINT "INFLUENCE COEFFICIENTS"
1810 PRINT "BKGD",A1
1815 FOR J= 1 TO J1
1820 PRINT J$(J),T(J)
1825 IF M<5 THEN 1835
1830 PRINT J$(J+6),T(J+6)
1835 NEXT J
1840 GO TO 1710
1845 PRINT "J2=";
1850 INPUT J2
1855 GO TO 390
1860 FOR I= 1 TO I1
1865 IF F(I)=1 THEN 1875

```

```

1870 LET C(I,J2)=D(I)
1875 NEXT I
1880 GO TO 1710
1885 PRINT"I,J=";
1890 INPUT I,J
1895 PRINT"F(I),C(I,J),Z(I,J),V(I,J) ="
1900 INPUT F(I),C(I,J),Z(I,J),V(I,J)
1905 GO TO 1710
1910 PRINT "" ,"CONCENTRATIONS"
1915 FOR I= I2 TO I3
1920 PRINT USING 1955,I,S$(I);
1925 FOR J= 1 TO J1
1930 PRINT USING 1960,C(I,J);
1935 NEXT J
1940 PRINT
1945 NEXT I
1950 GO TO 1710
1955: ### 'LLLL
1960: #####.##
1965 RETURN
1970 STOP
4990 DATA 7,0
5000 END

```

3477-282
Lot J

100-2
100-2





LIBRARY OF CONGRESS



0 002 959 668 2